

Liquid-phase veratrole acylation and toluene alkylation over WO_x/ZrO_2 solid acid catalysts

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Abstract

The liquid-phase acylation of veratrole with acetic anhydride and alkylation of toluene with 1-dodecene were carried out over WO_x/ZrO_2 solid acid catalysts. The catalysts were prepared by wet impregnation method using zirconium oxyhydroxide and ammonium metatungstate. Catalysts with different WO_3 loading (5–30 wt.%) were prepared and calcined at 800 °C and catalyst with 15% WO_3 was calcined from 650 to 850 °C. All the catalysts were characterized by nitrogen adsorption, XRD and NH_3 -TPD. The catalyst with 15% WO_3 calcined at 800 °C (15 WZ-800) was found to be the most active in acylation and alkylation reactions. The effect of temperature, molar ratio and catalyst weight on the conversions of acetic anhydride and dodecene were studied in detail. The catalyst 15 WZ-800 gave 67% acetic anhydride conversion in veratrole acylation under the reaction conditions of 70 °C, veratrole/acetic anhydride molar ratio 2, time 4 h and 99% dodecene conversion with >99% monododecyl toluene selectivity at 100 °C, toluene/1-dodecene molar ratio 10 and time 1 h.

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1. Introduction

Friedel–Craft acylation of aromatic compounds have generated continued interest due to their importance and versatility in the production of aromatic ketones largely used as intermediates in the synthesis of pharmaceuticals and fine chemicals [1–7]. Similarly, alkylations of aromatics with higher linear olefins are industrially important as these are used for the production of linear alkyl aromatics, which are used as the precursors in the production of biodegradable surfactants [8]. Acylation and alkylation of aromatics have traditionally been carried out using homogeneous acid catalysts such as AlCl_3 , FeCl_3 , ZnCl_2 , and HF, etc. [9–11]. But these catalysts are highly polluting, corrosive and are consumed in stoichiometric amounts in acylation reactions due to the formation of 1:1 molar adduct with aromatic ketones, which cannot be recovered and need to be neutralized creating large salt waste [12]. These salt wastes are hazardous, corrosive to equipment and non-ecofriendly. So, there

is long felt need and demand for replacement of conventional Lewis and Brønsted acids with easily recyclable and regenerable solid acid catalyst in view environmental limitations. Since, solid catalysts are easy to recover, reuse and overcome corrosion problems, which could replace conventional catalysts and these processes fit well in the domain of environmentally benign chemistry.

During the past few years, different solid acid catalyst such as zeolites [13] metal cation exchanged clays [14], ion exchange resins [15], and supported-heteropoly acids have been used for acylation of veratrole [16]. For the alkylation of toluene with 1-dodecene, large pore zeolites like H faujasite (HFAU), H mor-denite (HMOR) and H beta (HBEA) were used [17].

Zirconia-based solid acids are attracting much attention in recent years. For instance, sulfated zirconia proved to be a highly active solid acid catalyst for various organic transformations [18]. But, its poor stability and tendency to form volatile sulfur compounds during catalysis and regeneration limit its applicability [19]. However, zirconia-supported tungsten oxide, WO_x/ZrO_2 is shown to be an alternative to sulfated zirconia, which is stable at high temperature and in presence of both oxidizing and reducing atmosphere [20,21].

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The present work deals with acylation of veratrole by acetic anhydride and alkylation of toluene by 1-dodecene using WO_x/ZrO_2 as catalyst. The reactions were carried out with an aim to maximize the conversion of acetic anhydride to acylated product in acylation of veratrole, and monododecyl toluene in alkylation of toluene by 1-dodecene. The influence of WO_3 loading and catalyst calcination temperature over the catalyst performance in both the reactions has been studied. The catalyst with highest activity has been used to study the effect of reaction parameters, such as reaction temperature, molar ratio of the reactants and catalyst weight on the conversions and product selectivity in both the reactions.

2. Experimental

2.1. Chemicals

Zirconium oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$), ammonia (25%), acetic anhydride (98%) and toluene (99.5%) were procured from S.D. Fine chemicals Ltd. Mumbai. Veratrole (pyrocatechol dimethyl ether) was obtained from Merck (India) Ltd. Mumbai. Ammonium metatungstate hydrate ($(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$) and 1-dodecene were purchased from Aldrich. Zeolite USY (Si/Al=9) was provided by PQ Corporation. All the chemicals were research grade and were used as received without further purification.

2.2. Catalyst preparation

The catalysts were prepared by wet impregnation method using zirconium oxyhydroxide as the support and ammonium metatungstate as tungsten precursor. The support was prepared by the hydrolysis of an aqueous solution of zirconium oxychloride with aqueous NH_3 . The precipitate obtained was washed till free from chloride and dried at 120°C . To an aqueous solution of ammonium metatungstate, zirconium oxyhydroxide powder was added and the mixture was stirred for 8–10 h. The excess water was evaporated to dryness and the obtained product was dried at 120°C and calcined in air at different temperatures. A series of catalysts with different WO_3 loading (5–30 wt.% of zirconium oxyhydroxide) were prepared and calcined at 800°C . In order to study the influence of calcination temperature on catalytic activity, the catalyst 15% WO_3/ZrO_2 was calcined from 600 to 900°C . The catalysts are represented by $x\text{WZ-T}$, where, x represents wt.%, W represents tungsten oxide, Z represents zirconia and T denotes calcination temperature in $^\circ\text{C}$.

2.3. Characterization

The specific surface area of the catalysts was measured by N_2 physisorption at liquid nitrogen temperature using a Quanta chrome Nova-1200 surface area analyzer and standard multi point BET analysis methods. Samples were out gassed at 300°C in N_2 flow for 2 h before N_2 physisorption measurements.

X-ray diffraction (XRD) measurements of the catalyst powder were recorded using a Rigaku Geigerflex diffractometer

equipped with Ni filtered Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The volume percentage of tetragonal phase (V_t) of the calcined samples was estimated with the formula proposed by Toraya et al. [22].

$$X_m = \frac{I_m(11-1) + I_m(111)}{[I_m(11-1) + I_m(111) + I_t(111)]}$$

$$V_m = \frac{1.311 X_m}{[1 + 0.31 X_m]} \quad \text{and} \quad V_t = 1 - V_m$$

where, I_m (h k l) is the integral intensity of the (h k l) reflections of the monoclinic phase and I_t (1 1 1) the intensity of the (1 1 1) reflection of the tetragonal phase.

The nature of the acid sites (Brönsted and Lewis) of catalysts with different WO_3 loading was characterized by ex situ FTIR spectroscopy with chemisorbed pyridine. A freshly activated catalyst powder sample was saturated with pyridine vapors placed in a desiccator containing pyridine. The pyridine-saturated sample was then activated at 300°C for 2 h and the FTIR spectra of the samples were recorded on a Shimadzu (Model-820 PC) spectrophotometer under DRIFT (diffuse reflectance infrared Fourier transform) mode.

The acidity of the catalysts were measured by temperature programmed desorption of NH_3 (NH_3 -TPD) using a micromeritics AutoChem-2910 instrument. It was carried out after ~ 0.3 g of the catalyst sample was dehydrated at 500°C in He ($30 \text{ cm}^3 \text{ min}^{-1}$) for 1 h. The temperature was decreased to 100°C and NH_3 was adsorbed by exposing samples treated in this manner to a stream containing 10% NH_3 in He for 1 h at 100°C . It was then flushed with He for another 1 h to remove physisorbed NH_3 . The desorption of NH_3 was carried out in He flow ($30 \text{ cm}^3 \text{ min}^{-1}$) by increasing the temperature to 550°C at $10^\circ\text{C min}^{-1}$ measuring NH_3 desorption using TCD detector.

2.4. Catalytic activity measurements

The liquid-phase acylation and alkylation reactions were carried out under atmospheric pressure in 50 ml glass batch reactor. The reaction mixture containing a mixture of veratrole and acetic anhydride in acylation reaction and toluene/1-dodecene in alkylation reaction together with WZ catalyst were charged into the round bottom flask fitted with a reflux condenser and CaCl_2 guard tube, equipped with a magnetic stirrer and immersed in a thermostated oil bath. The catalyst was activated at 500°C for 2 h in flow of dry air and cooled to the reaction temperature prior to its use in the reaction. The clear solution of the reaction mixture was withdrawn periodically, centrifuged and analyzed by Shimadzu 14B gas chromatograph, equipped with a flame ionization detector using HP-5 capillary column (cross linked 5% ME silicone, $30 \text{ m} \times 0.53 \times 1.5 \mu\text{m}$ film thickness). The products were identified by GC-MS and by comparing with authentic samples. Conversions were defined as the conversion of acetic anhydride into ketone and dodecene into alkylated products in acylation and alkylation reactions, respectively.

3. Results and discussion

3.1. Characterization of the catalysts

3.1.1. Surface area

The pure zirconium oxyhydroxide dried at 120 °C showed a surface area of 331.6 m² g⁻¹. After calcination at 800 °C, the surface area decreased to 10 m² g⁻¹. Addition of WO₃ to the support results in an increase of the surface area, which becomes maximum at ca. 61 m² g⁻¹ for 15% WO₃ loading (Fig. 1). This can be explained as the added WO₃ strongly interact with zirconia that reduces the surface diffusion of zirconia and inhibits sintering [23] and stabilizes the tetragonal phase of zirconia, which leads to an increase in surface area. Above 15% WO₃ loading, XRD indicates the formation of crystalline WO₃, which probably narrows or plugs the pores of the samples, thus leading to the decrease in the specific surface area [24]. The WO₃ loading corresponding to each loading and calcination temperature is determined to calculate the nominal tungsten (W) surface density using the measured surface area. The tungsten surface densities, expressed as the number of W atoms per nanometer square area (W atoms nm⁻²) and were calculated using the equation: surface density of W = {[WO₃ loading (wt.)/100] × 6.023 × 10²³} / {[231.8 (formula weight of WO₃) × BET surface area (m² g⁻¹) × 10¹⁸]} and are given in Table 1. It is seen that an increase of WO₃ loading results in an increase of the W surface density. The specific surface area of WZ catalysts also depends on the calcination temperature. The W surface density increased with the calcination temperature, because of the concomitant decrease in the ZrO₂ surface area (Fig. 1).

3.1.2. X-ray diffraction

The XRD pattern of the catalysts with different WO₃ loading calcined at 800 °C (Fig. 1) showed that, the presence of WO₃

Table 1

Surface area, surface density, phase composition and acidity of various catalysts

| Sample | Surface area (m ² g ⁻¹) | Surface density (W nm ⁻²) | Vol.% <i>t</i> -ZrO ₂ | Acidity (NH ₃ nm ⁻²) |
|-----------|--|---------------------------------------|----------------------------------|---|
| Z-800 | 12 | 0 | 6 | n. e. |
| 5 WZ-800 | 38 | 3.9 | 9 | n. e. |
| 10 WZ-800 | 54 | 5.5 | 66 | 2.6 |
| 15 WZ-800 | 61 | 7.3 | 93 | 2.5 |
| 20 WZ-800 | 55 | 10.9 | 89 | 2.7 |
| 25 WZ-800 | 50 | 14.9 | 96 | 3.1 |
| 30 WZ-800 | 48 | 18.7 | 95 | n.e. |
| 15 WZ-700 | 84 | 5.3 | 100 | 3 |
| 15 WZ-750 | 70 | 6.4 | 95 | 2.6 |
| 15 WZ-850 | 44 | 10 | 19 | 3 |

n.e.: not evaluated.

strongly influences the crystallization of zirconium oxyhydroxide into zirconia. Pure zirconia calcined at 800 °C is mainly monoclinic with only a small amount of the tetragonal phase. For catalysts with low WO₃ loading calcined at 800 °C, the XRD pattern can be described as the sum of the monoclinic and tetragonal phases of zirconia, this latter phase becoming dominant for catalyst with 15% WO₃. The tetragonal content of zirconia at a fixed loading depends on the calcination temperature and for 15% catalyst, zirconia exists mainly in the tetragonal form up to 800 °C and the tetragonal content decreases with further increase in calcination temperature. At high calcination temperature, WO_x species agglomerate into monoclinic WO₃ crystallites and becomes less effective sintering inhibitors. Thus, the added WO₃ stabilizes the tetragonal phase of zirconia and such stabilization of tetragonal ZrO₂ in presence of WO₃ and other oxides has been reported in the literature [23,24]. It can also be seen that up to a 10% WO₃ loading for catalysts calcined at 800 °C and for 15% catalyst, up to 750 °C calcination, no diffraction lines, which could be attributed to crystalline WO₃, are observed, indicating that WO₃ is highly dispersed on the support. When

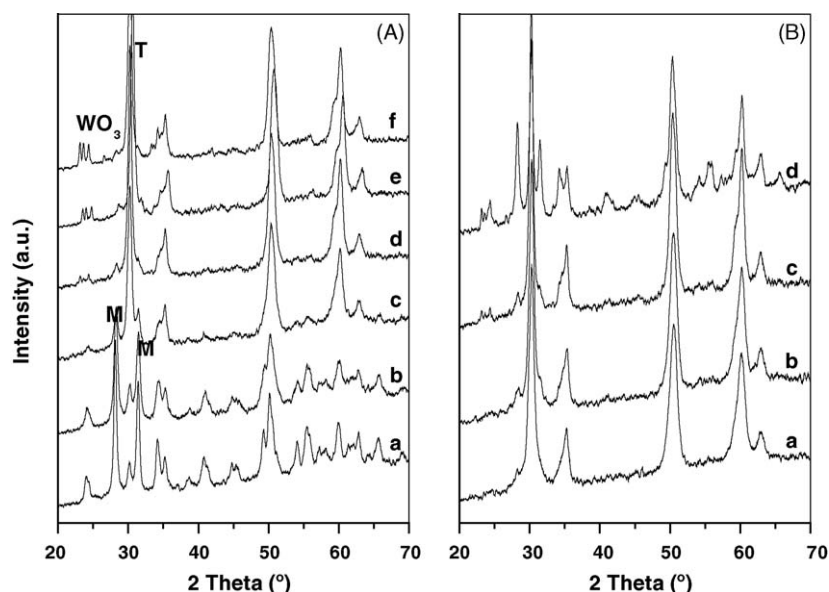


Fig. 1. X-ray diffractograms of (A) catalysts with different WO₃ loading (a) Z-800, (b) 5 WZ-800, (c) 10 WZ-800, (d) 15 WZ-800, (e) 20 WZ-800, (f) 25 WZ-800; and (B) 15 WZ catalyst calcined at different temperatures (a) 700, (b) 750, (c) 800, and (d) 850 °C.

WO₃ loading is higher than 10%, or when the calcination temperature exceeds 750 °C for 15% loading, new diffraction lines appear in the 2θ region of 23–25°, characteristic of monoclinic WO₃ [24]. Thus, when the tungsten surface density exceeds the theoretical monolayer capacity of ZrO₂ (7 nm⁻²), i.e., WO₃ loading exceeds monolayer coverage, X-ray diffractogram show the presence of bulk crystalline WO₃.

3.1.3. FTIR pyridine adsorption

Adsorption of pyridine as a base on the surface of solid acids is one of the most frequently applied methods for the characterization of surface acidity. The use of IR spectroscopy to detect adsorbed pyridine enables us to distinguish among different acid sites. FTIR pyridine adsorption spectra of catalysts with different WO₃ loading calcined at 800 °C are shown in Fig. 2. The catalysts showed Brønsted (B) and Brønsted (B)+Lewis (L) acidity at 1543 cm⁻¹ and at 1489 cm⁻¹, respectively [25].

3.1.4. TPD of NH₃

This adsorption–desorption technique permits the determination of the strength of acid sites present on the catalyst surface, together with total acidity. The TPD profiles of the catalysts with different WO₃ loading, the amounts of adsorbed NH₃ per square nanometer of the catalysts with different WO₃ loading and of catalyst with 15% WO₃ calcined at different temperatures are shown in Fig. 3. All samples show a broad TPD profile, revealing that the surface acid strength is widely distributed. It is evident from the data that there is an initial increase in the acidity up to 15% loading, and thereafter the acidity decreases. For 15% WZ catalysts, calcined at different temperatures, the amount of adsorbed ammonia increases with calcination temperature and reaches a maximum at 800 °C.

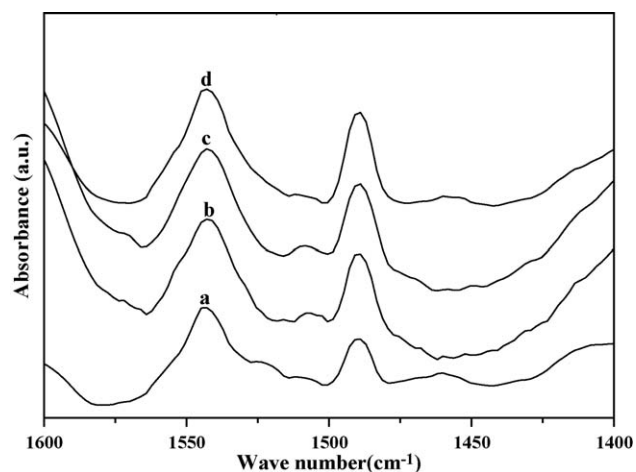
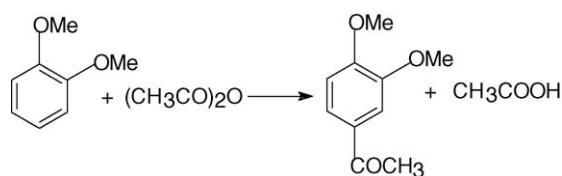


Fig. 2. FTIR pyridine adsorption spectra of catalysts with different WO₃ loading (a) 10 WZ-800, (b) 15 WZ-800, (c) 20 WZ-800, (d) 25 WZ-800.



Scheme 1.

3.2. Veratrole acylation

The acylation of veratrole with acetic anhydride gave aceto-veratrone (3,4-dimethoxy acetophenone) as the acylated product (Scheme 1). The conversion is expressed as the percentage of acetic anhydride converted into the acylated product.

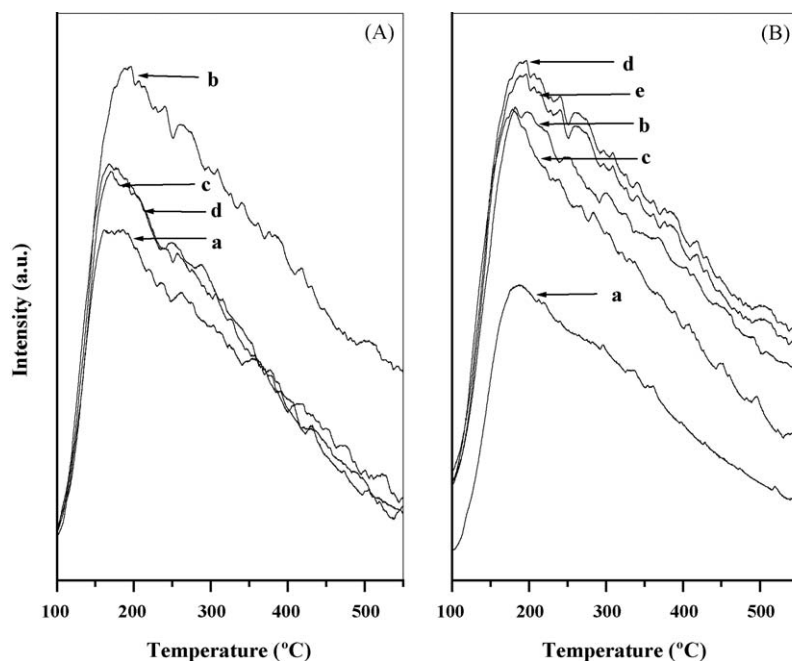


Fig. 3. NH₃-TPD profiles of (A) catalysts with different WO₃ loading (a) 10 WZ-800, (b) 15 WZ-800, (c) 20 WZ-800, (d) 25 WZ-800; and (B) 15 WZ catalyst calcined at different temperatures (a) 650, (b) 700, (c) 750, (d) 800, (e) 850 °C.

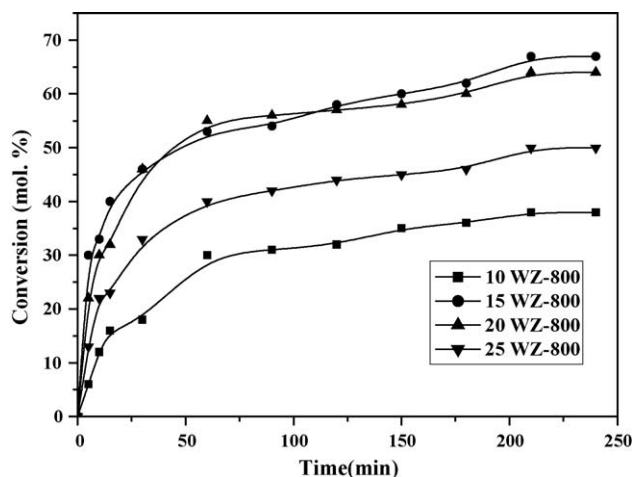


Fig. 4. Effect of WO_3 loading on Ac_2O conversion (reaction conditions: reaction temperature, 70°C ; total weight of the reaction mixture, 10 g; veratrole/ Ac_2O molar ratio = 2; catalyst weight, 3 wt.% of the reaction mixture).

In order to investigate the effect of WO_3 loading, 5–30 WZ-800 catalysts are used in acylation of veratrole with acetic anhydride (Ac_2O) at 70°C (Fig. 4). Among the catalysts with different WO_3 loading, the catalyst 5 WZ-800 showed no acetic anhydride conversion, while the catalyst 15 WZ-800 gave the highest conversion (67%). Further, increase in WO_3 loading decreases the Ac_2O conversion and for 25 WZ it is 50%.

The catalyst 15 WZ calcined different temperatures are used to study the change in catalytic activity with calcination temperature. It is clear from Fig. 5, that calcination temperature has a profound effect on the catalytic activity. The catalyst calcined at 650°C shows 31% conversion of acetic anhydride, which increases to 67% after calcination at 800°C . Further increase in catalyst calcination temperature, decreases Ac_2O conversion.

The initial reaction rate versus tungsten surface density for catalysts with different WO_3 loading calcined at 800°C and 15 WZ catalyst calcined at different temperatures in acylation of

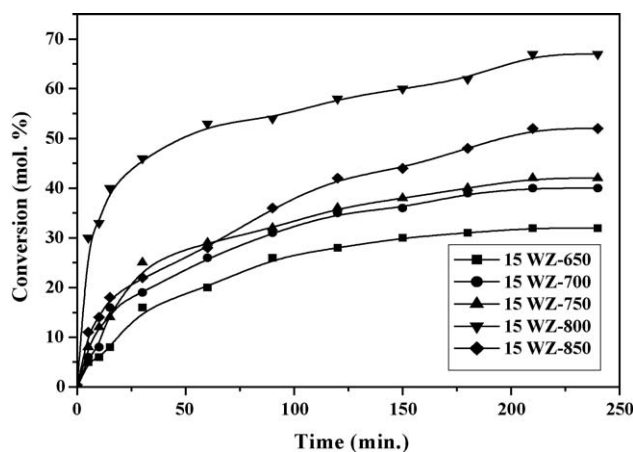


Fig. 5. Effect of catalyst calcination temperature on Ac_2O conversion (reaction conditions: temperature, 70°C ; total weight of the reaction mixture, 10 g; veratrole/ Ac_2O molar ratio = 2; catalyst weight, 3 wt.% of the reaction mixture).

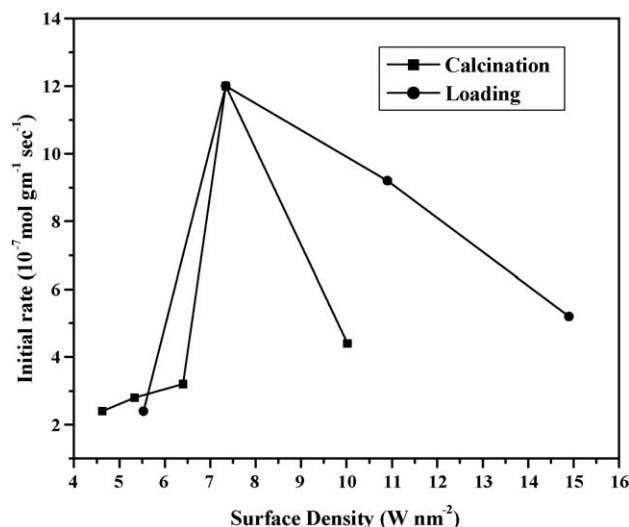


Fig. 6. Initial reaction rate vs. tungsten surface density of catalysts with different WO_3 loading calcined at 800°C and 15 WZ catalyst calcined at different temperatures.

veratrole is shown in Fig. 6. The change in initial reaction rate with loading and calcination temperature shows that the catalyst 15 WZ-800 has the highest catalytic activity. The surface density of 15 WZ-800 catalyst is found to be 7.34 W nm^{-2} , which is slightly higher than the monolayer coverage of WO_3 on zirconia. Iglesia and co-workers, from in situ acidity measurements showed that Brønsted acidity of WZ catalysts increases up to monolayer coverage of WO_3 on zirconia [26]. At high W surface densities, XRD shows the presence of bulk crystalline WO_3 and hence the active sites are inaccessible to the reactants and this decreases the catalytic activity. The highest catalytic activity at surface density of 7.3 W nm^{-2} clearly indicated that irrespective of WO_3 loading and calcination temperature, catalytic activity depended on WO_3 coverage and the catalyst with WO_3 loading slightly higher than that required for monolayer coverage had the highest catalytic activity.

Thus, the catalyst with highest activity is used to study different reaction parameters. The reaction is studied in the temperature range of 50 – 90°C using the most active catalyst 15 WZ-800 (Fig. 7). At 50°C , Ac_2O conversion is 22% and it increases to 67% at 70°C . Further increase in reaction temperature to 90°C has no appreciable effect on Ac_2O conversion. The effect of molar ratio on Ac_2O conversion is studied at 70°C with veratrole/ Ac_2O molar ratio of 1:3 (Fig. 8). At a molar ratio of 1, conversion is 25%, which increased to 67% at a molar ratio of 2. Further increase in molar ratio has no appreciable effect in Ac_2O conversion. The effect of catalyst weight on Ac_2O conversion was studied using 1–5% (Fig. 9) of total weight of the reaction mixture as catalyst. The 1-wt.% catalyst concentration gave Ac_2O conversion of 21% and it increased to 67% with 3 wt.% catalyst concentrations.

In order to study the recyclability of the catalyst, the reaction was conducted at 70°C with 3 wt.% catalyst using veratrole/acetic anhydride molar ratio 2 for 2 h. Fresh catalyst showed 58% Ac_2O conversion in 2 h. For recycling, the catalyst used in

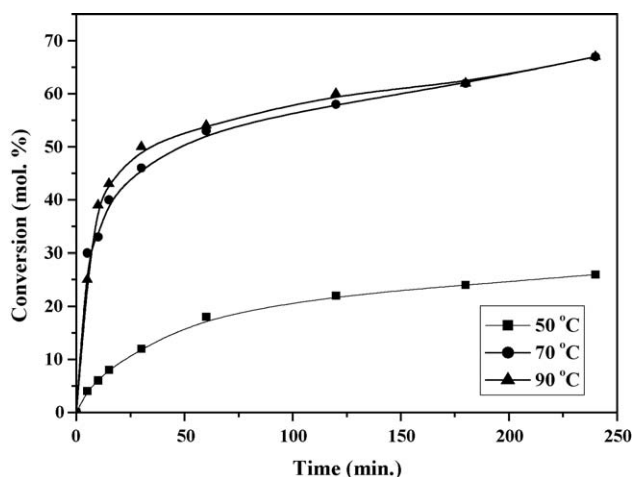


Fig. 7. Effect of reaction temperature on Ac_2O conversion (reaction conditions: total weight of the reaction mixture, 10 g; veratrole/ Ac_2O molar ratio = 2; catalyst weight, 3 wt.% of the reaction mixture).

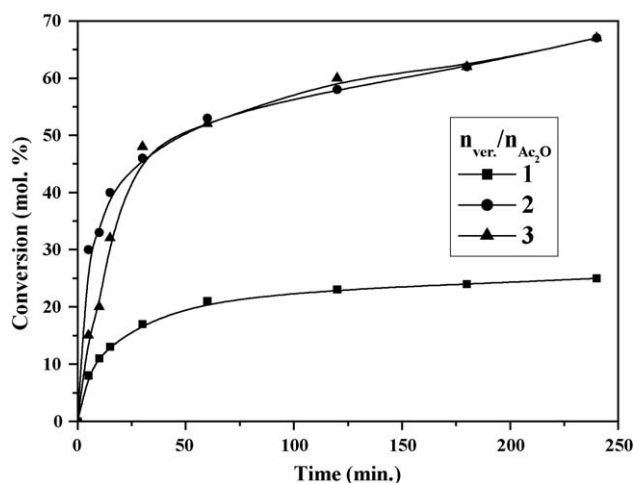


Fig. 8. Effect of veratrole/ Ac_2O molar ratio on Ac_2O conversion (reaction conditions: temperature, 70 °C; total weight of the reaction mixture, 10 g; catalyst weight, 3 wt.% of the reaction mixture).

the first cycle was separated by filtration, washed with methanol and dried at 100 °C for 3 h and rerun with fresh reaction mixture. The methanol washed catalyst showed 16% Ac_2O conversion in 2 h. The lower activity of the separated catalyst after washing may be due to the presence of surface bound acetate species formed from the by-product acetic acid, which is difficult to remove by washing [27,28]. However, after regeneration of the catalyst by calcination, Ac_2O conversion was increased to 53%. The activity loss observed with the regenerated catalyst could

be due to partial loss of acid sites of the catalyst during reaction/regeneration.

Finally the activity of 15 WZ-800 catalyst is compared with that of zeolite HY in acylation of veratrole with acetic anhydride at 90 °C for 2 h using veratrole/ Ac_2O molar ratio of 1 and catalyst concentration of 1 wt.% of total weight of the reaction mixture. The HY zeolite gave 63% Ac_2O conversion, while 15 WZ-800 catalyst gave 56% Ac_2O conversion. Thus, the activity of 15 WZ-800 catalyst is slightly lower than that of zeolite HY.

Table 2
Effects of different parameters on WZ catalyzed alkylation of toluene by 1-dodecene

| No. | Catalyst | Toluene/1-dodecene molar ratio | Catalyst weight (%) ^a | Reaction temperature (°C) | Conversion of dodecene (%) |
|--|----------|--------------------------------|----------------------------------|---------------------------|----------------------------|
| (A) Effect of WO_3 loading | | | | | |
| 1 | 10WZ-800 | 10:1 | 5 | 90 | 15 |
| 2 | 15WZ-800 | 10:1 | 5 | 90 | 49 |
| 3 | 20WZ-800 | 10:1 | 5 | 90 | 40 |
| 4 | 25WZ-800 | 10:1 | 5 | 90 | 38 |
| (B) Effect of catalyst calcination temperature | | | | | |
| 5 | 15WZ-650 | 10:1 | 5 | 90 | 3 |
| 7 | 15WZ-700 | 10:1 | 5 | 90 | 12 |
| 8 | 15WZ-750 | 10:1 | 5 | 90 | 45 |
| 9 | 15WZ-800 | 10:1 | 5 | 90 | 49 |
| 10 | 15WZ-850 | 10:1 | 5 | 90 | 23 |
| (C) Effect of reaction temperature | | | | | |
| 11 | 15WZ-800 | 10:1 | 5 | 80 | 9 |
| 12 | 15WZ-800 | 10:1 | 5 | 90 | 49 |
| 13 | 15WZ-800 | 10:1 | 5 | 100 | 99 |
| (D) Effect of toluene/1-dodecene molar ratio | | | | | |
| 14 | 15WZ-800 | 2.5:1 | 5 | 90 | 18 |
| 15 | 15WZ-800 | 5:1 | 5 | 90 | 21 |
| 16 | 15WZ-800 | 7.5:1 | 5 | 90 | 36 |
| 17 | 15WZ-800 | 10:1 | 5 | 90 | 49 |
| (E) Effect of catalyst weight | | | | | |
| 18 | 15WZ-800 | 10:1 | 1 | 90 | 26 |
| 19 | 15WZ-800 | 10:1 | 3 | 90 | 28 |
| 20 | 15WZ-800 | 10:1 | 5 | 90 | 49 |
| 21 | 15WZ-800 | 10:1 | 7 | 90 | 67 |

Conditions: total weight of the reaction mixture, 10 g; time, 1 h, ^acatalyst weight with respect to total weight of the reaction mixture.

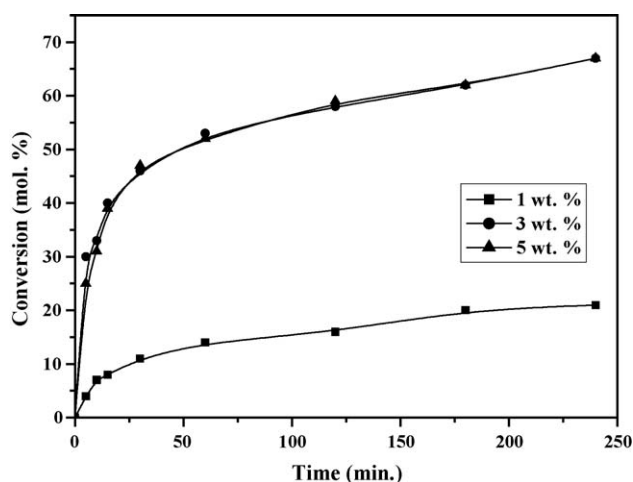


Fig. 9. Effect of catalyst weight on Ac_2O conversion (reaction conditions: temperature, 70°C ; total weight of the reaction mixture, 10 g; veratrole/ Ac_2O molar ratio = 2).

3.3. Alkylation of toluene by 1-dodecene

The main reactions obtained with these catalysts were alkene double bond shift isomerization and toluene alkylation giving monododecyltoluene as the alkylated product. The formation of dialkylated products was not observed under the reaction conditions studied here. The conversion was expressed as the percentage of alkene converted into alkylated products. The effect of WO_3 loading on dodecene conversion was investigated using 10–25 WZ-800 catalysts with toluene to 1-dodecene molar ratio of 10 at 90°C for 1 h (Table 2). The 15WZ-800 catalyst shows dodecene conversion of 49% and 25 WZ-800 catalyst gave 38% conversion under the reaction conditions studied. It is clear that calcination temperature has a profound effect on conversion of dodecene. The 15 WZ-650 catalyst gave very low dodecene conversion and the conversion increased to 49% with 15 WZ-800 catalyst (Table 2). The highest catalytic activity at surface density of 7.3 W nm^{-2} clearly indicated that irrespective of WO_3 loading and calcination temperature, catalytic activity depended on WO_3 coverage.

The catalyst with highest activity 15 WZ-800 used to study different reaction parameters. The effect of reaction temperature on dodecene conversion was studied from 80 to 100°C (Table 2). As expected, the conversion of dodecene increased with an increase in temperature and reached 99% with >99% monododecyltoluene selectivity at 100°C (Table 2). As the toluene/1-dodecene molar ratio increased from 2.5 to 10, conversion of dodecene increased from 18 to 49%, and further increase in molar ratio to 12, had no appreciable effect. The conversion of dodecene was 26% with 1 wt.% catalyst (total weight of the reaction mixture), which increased to 67% with 7 wt.% catalyst.

4. Conclusions

The liquid-phase acylation of veratrole with acetic anhydride and alkylation of toluene with 1-dodecene were studied using

WO_x/ZrO_2 catalyst. The most active catalyst 15 WZ-800 gave 67% acetic anhydride conversion in veratrole acylation under the reaction conditions of 70°C , veratrole/acetic anhydride molar ratio 2, time 4 h and 99% dodecene conversion with >99% monododecyl toluene selectivity at 100°C , toluene/1-dodecene molar ratio 10 and time 1 h. The 15 WZ-800 catalyst shows slightly lower activity than that of HY zeolite in acylation of veratrole. This catalyst system is easy to prepare and the deactivated catalyst can be reused without appreciable loss in catalytic activity after regeneration by calcination.

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References

- [1] G.A. Olah, Friedel–Crafts Chemistry, Wiley, New York, 1973.
- [2] G. Franck, J.W. Stadelhofer, Industrial Aromatic Chemistry, Springer-Verlag, Berlin, 1988.
- [3] P.J. Harrington, E. Lodewijk, Org. Process Res. Develop. 1 (1997) 72.
- [4] R.A. Sheldon, Chem. Ind. 7 (1992) 903.
- [5] G. Harvey, G. Mader, Collect. Czech. Chem. Commun. 57 (1992) 862.
- [6] H. Goda, M. Kawamura, K. Kato, M. Sato, US Patent 4,792,612 (1988).
- [7] T. Fujisawa, K. Kondo, K. Sakai, US Patent 4,266,067 (1981).
- [8] B.M. Devassy, F. Lefebvre, S.B. Halligudi, J. Catal. 231 (2005) 1.
- [9] P.H. Gore, in: G.A. Olah (Ed.), Friedel–Crafts and Related Reactions, vol. III, Wiley/Interscience, New York, 1964, p. 64.
- [10] B.S. Furniss, A.J. Hannaford, P.W.G. Smith, A.R. Tatchell, Vogel's Text Book of Practical Organic Chemistry, fifth ed., Longman, Singapore, 1989.
- [11] Kirk-Othmer, Encyclopedia of Chemical Technology, vol. 24, fifth ed., 1997, p. 38.
- [12] M.L. Kantam, K.V.S. Ranganath, M. Sateesh, K.B.S. Kumar, B.M. Chaudary, J. Mol. Catal. A 225 (2005) 15.
- [13] C. Guinard, V. Pedron, F. Richard, R. Jacquot, M. Spagnol, J.M. Coustard, G. Perot, Appl. Catal. A 234 (2002) 79.
- [14] B.M. Choudary, M. Sateesh, M.L. Kantam, K.V.R. Prasad, Appl. Catal. 171 (1998) 55.
- [15] B.M. Choudary, M.L. Kantam, M. Sateesh, K.K. Rao, P.L. Santhi, Appl. Catal. A 149 (1997) 257.
- [16] G.D. Yadav, H.G. Manyer, Microp. Mesop. Mater. 63 (2003) 85.
- [17] Z. Da, Z. Han, P. Magnoux, M. Guisnet, Appl. Catal. A 219 (2001) 45.
- [18] G.D. Yadav, J.J. Nair, Microp. Mesop. Mater. 33 (1991) 1.
- [19] R. Sreenivasan, R.A. Keogh, D.R. Milburn, B.H. Davis, J. Catal. 153 (1995) 123.
- [20] M. Hino, K. Arata, J. Chem. Soc. Chem. Commun. (1998) 1259.
- [21] S. Kuba, P. Lukinskas, R.K. Grasselli, B.C. Gates, H. Knozinger, J. Catal. 216 (2003) 353 (and references therein).
- [22] H. Toraya, M. Yoshimura, S. Somiya, J. Am. Ceram. Soc. 67 (1984) C119.
- [23] E. Iglesia, S.L. Soled, G.M. Kramer, J. Catal. 144 (1993) 238.
- [24] F.D. Gregorio, V. Keller, J. Catal. 225 (2005) 45.
- [25] R. Sakhivel, H. Perscott, E. Kemnitz, J. Mol. Catal. A: Chem. 223 (2004) 137.
- [26] J. Macht, C.D. Baertsch, M. May-Lozano, S.L. Soled, Y. Wang, E. Iglesia, J. Catal. 227 (2004) 470.
- [27] B. Bachiller-Baeza, J.A. Anderson, J. Catal. 228 (2004) 225.
- [28] A. Trunschke, J. Deutsch, D. Müller, H. Lieske, V. Quaschnig, E. Kemnitz, Catal. Lett. 83 (2002) 271.